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Wiebinga, C.J.; Baar, H.J.W. de

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Determination of the distribution of dissolved organic carbon in the Indian sector of the Southern Ocean

C.J. Wiebinga^{*}, H.J.W. de Baar

Netherlands Institute for Sea Research (NIOZ), P.O. Box 59, 1790 AB Den Burg, Texel, Netherlands

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Abstract

During France JGOFS campaign ANTARES 2 (R.V. *Marion Dufresne*), samples were taken along a section of the 62°E meridian from 49° to 66°S. The high temperature catalytic oxidation (HTCO) method was used to determine the concentration of dissolved organic carbon (DOC). The analyses were conducted both on-board ship and after the cruise in the laboratory. Collecting and storing acidified samples for post-cruise analysis induced no significant differences. The use of two separate but identical channels on the carbon analyzer increased the number of samples analysed per day and allowed independent monitoring of the instrument blank and the calibration of the detector response. The mixed layer concentrations of organic carbon varied from about 52 $\mu\text{M C}$ in the Antarctic Divergence (64°S) to about 63 $\mu\text{M C}$ in the Polar Frontal Zone (49°S). Vertical profiles showed a slight, but significant, decrease in organic carbon below the mixed layer, to about 42 $\mu\text{M C}$ below 2000 m across the transect. The homogeneity and low concentration of organic carbon in deep water is consistent with values recently reported for the equatorial Atlantic and Pacific Ocean and supports the evidence for a constant deep water DOC concentration. In addition, this provides a verification of the instrument performance, thus validating observed DOC data trends and allowing a comparison with the 'modern' DOC literature. In general, the organic carbon concentration in the mixed layer was lower than previously published data of the main ocean basins, which might reflect the low chlorophyll *a* concentration ($< 0.5 \mu\text{g/l}$) encountered in this region. Along the 62°E meridian section, organic carbon showed a trend with corresponding measurements of phytoplankton biomass and bacterial production, underlining the dependence of bacterial growth on a pool of 'freshly' produced DOC. Organic carbon was found to exhibit a weak inverse trend versus apparent oxygen utilization (AOU). This suggests that only a small part of the oxygen consumption is due to the mineralisation of DOC. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: dissolved organic carbon (DOC); apparent oxygen utilization (AOU); bacterioplankton; mineralisation

1. Introduction

The oceans contain a very dilute, but in absolute amount, large pool of DOC, equivalent to the carbon

in the atmosphere ($750 \times 10^{15} \text{ gC}$; Williams, 1975). Although numerous studies have been dedicated to this topic, the sources and fate of this large carbon pool are still in debate. The presumable role in biogeochemical processes make DOC an important variable in global carbon cycling (Kirchman et al., 1991; Toggweiler, 1992). DOC consists of a mixture of compounds with varying reactivities and turnover

^{*} Corresponding author. Tel.: +31-222-369438; fax: +31-222-319674; e-mail: cas@nioz.nl

times (Ogawa and Ogura, 1992; Taylor et al., 1985; Amon and Benner, 1994). Based on the equal distribution over the world oceans and experimental evidence of resistance to microbial degradation (Barber, 1968), the bulk of DOC present in deep water is assumed to be relatively resistant to biochemical oxidation. This is consistent with the apparent old radiocarbon ages of 4000–6000 years for DOC (Williams and Druffel, 1987). Below the mixed layer, processes like respiration and decomposition of organic matter appear to have minimal effect on the in situ concentrations of oxygen and DOC, since often a weak or insignificant correlation between DOC and Apparent Oxygen Utilization (AOU) is found (Menzel and Ryther, 1968; Martin and Fitzwater, 1992; Thomas et al., 1995).

Elevated concentrations of DOC in the upper few hundred meters compared to deep water indicates in situ biological production of DOC in the euphotic zone. The terrestrial DOC inputs into the open oceans are relatively small as was revealed by isotopic signatures (Williams and Druffel, 1987). Primary production is the ultimate source of DOC production, but the exact mechanisms are still under investigation. According to Sharp (1977), the degradation of old and dying phytoplankton is the major source of organic matter in the sea, rather than direct excretion by phytoplankton. Sloppy feeding and zooplankton excretion are also mechanisms which may lead to DOC production (Taylor et al., 1985).

Incubation experiments demonstrate that there is a broad continuum of lability of DOC, with turnover rates ranging from hours to millennia (Barber, 1968; Ogura, 1972; Kroer, 1993). A small fraction of DOC in surface water constitutes highly labile organic compounds, such as dissolved free amino acids and sugars, which are readily available carbon sources for bacterioplankton. Rapid DOC turnover by bacterioplankton has been reported in several studies (Taylor et al., 1985; Kirchman et al., 1991; Amon and Benner, 1994; Hansell et al., 1995; Carlson and Ducklow, 1996). In addition, large (10–50 $\mu\text{M C}$) changes in DOC concentrations have been observed in situ in spring phytoplankton blooms in the North Atlantic Ocean and North Sea (Cadée, 1986; Kirchman et al., 1991; Lochte et al., 1993). Such DOC variations, far in excess of primary production rates, even when they actually represent patchiness, can

only be explained by high production and turnover rates of DOC.

Duursma (1963) observed seasonal changes of DOC in the North Sea, implying that a large fraction of DOC turns over in less than a year but more than days. Time series in the Mediterranean and Sargasso Sea revealed that DOC is accumulated during spring and advected to deeper water by wintermixing, resulting in an annual flux of DOC from the euphotic zone equal to or greater than the annual particle flux (Copin-Montégut and Avril, 1993; Carlson et al., 1994). In contrast, minimal daily, seasonal and fine scale vertical variations were observed in the equatorial Pacific Ocean (Carlson and Ducklow, 1995) indicating a tight coupling between DOC production and consumption. The net result is little accumulation and export of labile DOC. Changes in the distribution of DOC in the Central Equatorial Pacific surface waters appear to be driven by lateral input and equatorial upwelling (Peltzer and Hayward, 1996).

Taking into account the bulk of available descriptive data, none of the above postulations can unequivocally explain the oceanic DOC distribution. Most 'older' data is biased by a relatively large variation, possibly obscuring any relations with biological and/or physical observations. Also some of the early HTCO-data is suspect due to analytical problems. This is illustrated by the wide range of deep ocean DOC reported over the last decade, since there is no reasonable argument today for such large oceanic variability. This implies that not only some of the absolute DOC values are suspect, but also relative changes or variability might be biased by analytical problems in some studies.

Here we report estimates of DOC abundances in an area from the Antarctic Continent reaching into the Polar Frontal Zone (PFZ), as part of the France JGOFS studies in the Southern Ocean. The region covers (from south to north): the Coastal and Continental Shelf Zone (CCSZ), the Seasonal Ice Zone (SIZ) and the Permanently Open Ocean Zone (POOZ) bounded to the north by the Polar Front. The Southern Ocean, a known sink for atmospheric CO_2 , plays an important role in global carbon cycling. It is the world largest 'high nutrient low chlorophyll' region, which exhibits increased productivity only in the Polar Front, due to the entrainment of trace elements

(De Baar et al., 1995). These waters are characterized by regenerated production, with close coupling between production and consumption. Large export production is restricted to events of massive diatom blooms, superimposed on the general low background production (Smetacek et al., 1990; De Baar and Boyd, 1998). Our objectives are to assess the stocks and distribution of DOC over the water column with emphasis on the upper mixed layer where production occurs. Clean sampling techniques were used and precautions were taken to prevent contamination during sample handling and analysis. Because of the present uncertainties with DOC analysis (Williams, 1992; Sharp, 1993) and in order to validate our DOC values, a detailed description and evaluation of the analytical procedure, blank correction and instrument performance is given.

2. Materials and methods

During France JGOFS campaign ANTARES 2 (R.V. *Marion Dufresne*, 26 January 1994–23 March 1994) sampling was carried out in the Indian sector of the Southern Ocean. Along a section of the 62°E meridian, from 49° to 66°S, samples were taken at the stations indicated in Fig. 1. Two additional stations (52°S, 62°E and 63°S, 70°E) were occupied for several days, allowing sampling at one site during successive days. The positions of the stations are listed in Table 1. Overall sampling efforts and preliminary results have been reported by Fiala (1995).

2.1. Sampling

Discrete water samples were taken from a CTD rosette sampler (Seabird) equipped with 12 Niskin bottles (12 l) or from special casts with GOFLO bottles on a Kevlar wire. The latter were conducted for ultra-clean sampling of trace metals, described in detail by Sarthou et al. (1997). At each station both a shallow (0–300 m) and deep (> 300 m) CTD-cast were sampled, enhanced by in total 7 GOFLO casts at selected stations. Weather conditions encountered at station A16 precluded operation of the CTD.

Subsamples were drawn from the Niskin bottles into 250 ml PTFE bottles, directly after the gas sampling. Sample bottles were acid washed and left overnight filled with Milli-Q water before use. Prior

to sampling, bottles were carefully rinsed three times with seawater. As suggested by Peltzer and Brewer (1993) samples were drawn from the Niskin bottles by allowing the water to flow through the air without the use of any tubing and care was taken that the sample bottle did not come into contact with the sampling port of the Niskin bottle. Samples were put on ice and taken into a 'clean lab' container. Further sample handling was carried out in a laminar flow bench.

For the determination of total organic carbon (TOC), duplicate 8 ml samples (unfiltered) were acidified with three drops of concentrated phosphoric acid (45% w/v) and sealed in 10 ml ampoules. Samples taken from the shallow casts (0–300 m) were also filtered onto 0.2 μm polycarbonate filters (Poretics, 47 mm) in a polycarbonate filtration set-up (Sartorius). For each sample, 150 ml was filtered of which the first 50 ml were used to rinse the filter and the filtration set-up, and then discarded. The filter was replaced between samples. From the remaining 100 ml, duplicate 16 ml samples were acidified and sealed in 20 ml ampoules for the determination of dissolved organic carbon (DOC). Samples were stored at 5°C for later analysis. Part of the samples were analysed onboard and the remainder were analysed at the shore laboratory over the course of a year. The procedure of storing acidified samples sealed in ampoules at 5°C was established and shown to effectively preserve DOC by Hedges et al. (1993) and supported by Tupas et al. (1994).

2.2. Dissolved organic carbon analysis

A high temperature catalytic oxidation (HTCO) method was used for the determination of TOC and DOC concentrations. The HTCO is based on the method described by Sugimura and Suzuki (1988). A modified Ionics Model 555 carbon analyzer, with a pure platinum gauze catalyst at 775°C, was used for direct conversion of DOC to CO₂. Triplicate samples of 100 μl were injected manually into a quartz tube containing the catalyst. The catalyst consisted of pillow shaped gauze sheets covered by an unfolded sheet to prevent the pillows from moving during sample injection, presumably improving peak shape (Suzuki et al., 1992). A stream of ultra-pure oxygen gas, at a flow rate of 120 ml/min, carried water vapour and combustion gases through a series of

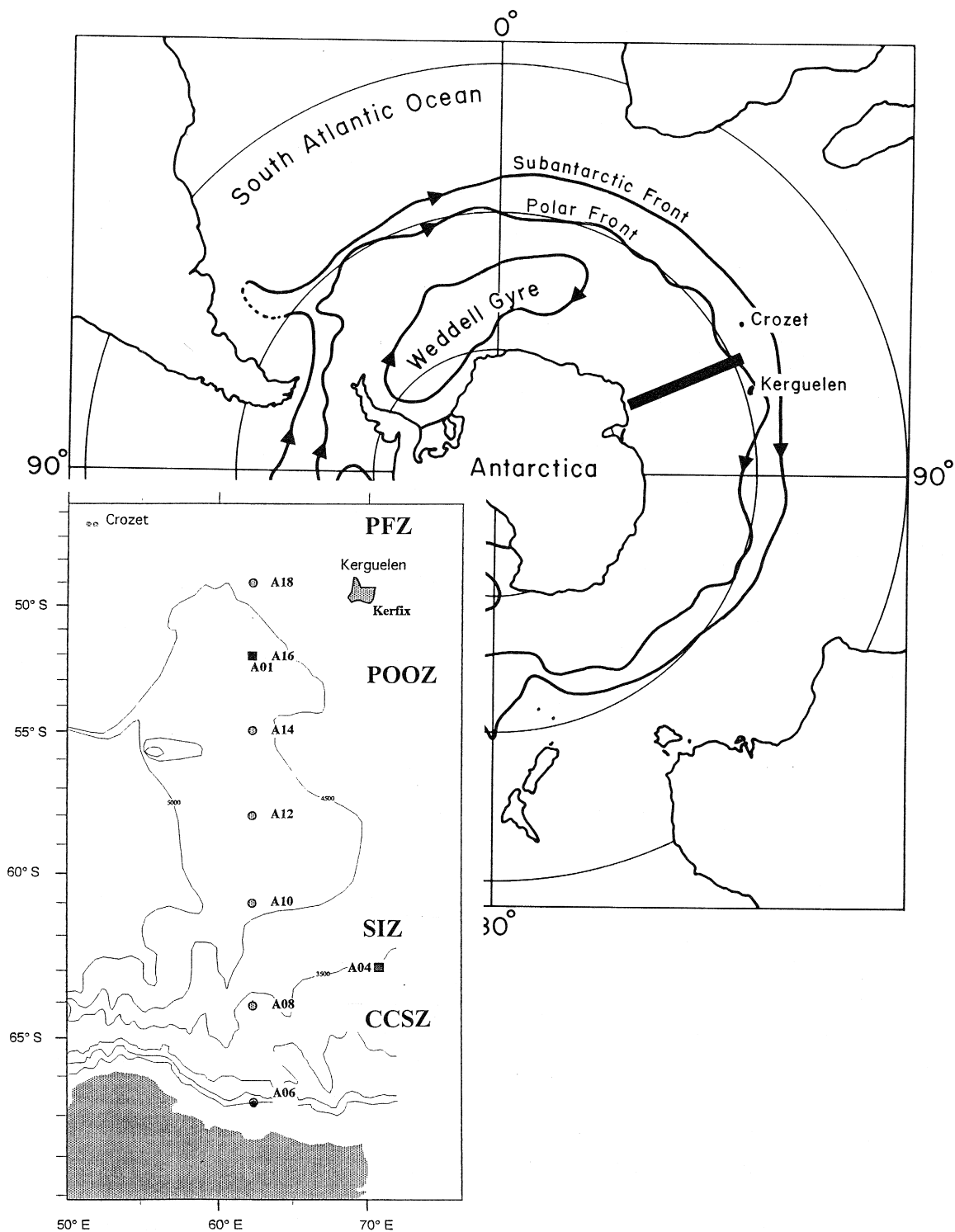


Table 1

Stations sampled during the ANTARES 2 cruise onboard the R.V. *Marion Dufresne*

Station	Cast	Date	Local time	Latitude	Longitude	Depth (m)
A01	CTD 01 S	10-Feb-94	19:44	52.01 S	62.00 E	2180
A01	CTD 04 P	11-Feb-94	0:46	52.05 S	61.59 E	2180
A01	GOFLO 1	13-Feb-94	4:30	52.00 S	62.00 E	
A01	GOFLO 2	13-Feb-94	22:00	52.00 S	62.00 E	
A04	CTD 21 P	18-Feb-94	23:13	63.00 S	70.34 E	4005
A04	GOFLO 3	19-Feb-94	19:00	63.00 S	70.38 E	
A04	GOFLO 4	20-Feb-94	5:00	63.00 S	70.38 E	
A04	CTD 23 S	22-Feb-94	1:04	63.13 S	70.13 E	3920
A06	CTD 30 P	24-Feb-94	16:07	66.42 S	61.50 E	
A06	CTD 31 S	24-Feb-94	18:28	66.41 S	61.49 E	900
A08	CTD 35 S	26-Feb-94	17:10	63.59 S	61.59 E	4087
A10	CTD 40 P	28-Feb-94	12:23	60.59 S	62.03 E	
A10	CTD 41 S	28-Feb-94	18:25	61.00 S	62.06 E	4620
A10	GOFLO 5	1-Mar-94	4:00	61.00 S	62.00 E	
A12	CTD 45 S	2-Mar-94	15:13	58.00 S	62.01 E	4870
A12	CTD 47 P	2-Mar-94	20:33	58.03 S	62.05 E	4725
A14	CTD 51 S	4-Mar-94	11:08	55.01 S	62.01 E	4700
A14	CTD 52 P	4-Mar-94	16:39	55.02 S	62.06 E	
A14	GOFLO 6	5-Mar-94	3:30	55.00 S	62.00 E	
A18	CTD 58 P	8-Mar-94	19:11	48.59 S	62.00 E	
A18	GOFLO 7	9-Mar-94	4:00	49.00 S	62.00 E	
A18	CTD 59 S	9-Mar-94	9:02	48.57 S	61.52 E	2610

traps (cold trap on ice, tin scrubber, anhydron and Balston® filter), before entering a Li-Cor Model LI-6252 CO₂-analyzer (Fig. 2). The signal, generated by the non-dispersive infrared (NDIR) detection of CO₂, was recorded and quantified as peak area on a Shimadzu Model C-R6A integrator and/or using XCHROM® software package. Peaks were typically 60 s wide at baseline, symmetric with a single maximum, but exhibited a slight tailing. After each analytical run, all individual peaks were visually checked and only peaks of which the shape deviated were omitted.

Ampoules were opened just before analysis and kept in a laminar flow bench to avoid airborne contamination. Prior to injection each sample was purged for 6 min with nitrogen gas at a flow rate of approximately 160 ml/min to remove inorganic carbon. After each triplicate seawater injection the column was flushed three times with 100 µl Milli-Q

water by injection with an automatic injector (Gilson Dilutor 401; equipped with a 0.5 ml syringe). This effectively prevented salt build-up on the catalyst. Typical processing time was 12 min per sample (including Milli-Q wash step). Combustion tubes with catalyst were replaced after approximately 1000 seawater injections. The catalyst was regenerated by boiling for several hours in concentrated nitric acid (65% w/v), rinsing with Milli-Q and drying under air followed by heating with a butane flame to a dull red. After cooling the Pt-gauze was packed in a new quartz column, which was mounted in the analyzer. Extensive conditioning of the combustion tubes was performed by repetitive injections of Milli-Q.

The original analyzer consisted of a TC-channel (at 800°C) and a separate IC-channel (at 150°C) for the determination of organic and inorganic carbon, respectively. We converted the IC-channel into a TC-channel equipped with an independent series of

Fig. 1. Position of the stations sampled during the ANTARES 2 cruise. Regions: Polar Front Zone (PFZ), Permanent Open Ocean Zone (POOZ), Seasonal Ice Zone (SIZ) and Coastal and Continental Shelf Zone (CCSZ). Fronts between regions are the Polar Front around 52°S and the Antarctic Divergence between 63°–64°S.

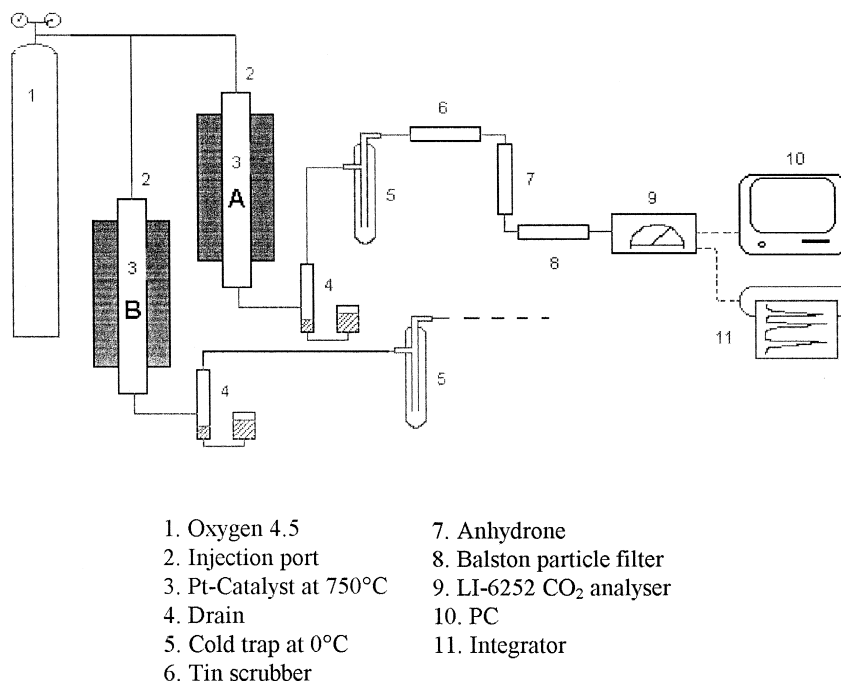


Fig. 2. Diagram of the modified Ionics 555 carbon analyzer used in this study.

traps, CO₂-analyser and integrator. This modification allowed simultaneous injection on two identical but independent lines (system A and B), doubling the number of samples analysed per day. In general both systems were operational and on each a set of samples (e.g., cast) was analysed. Regularly, a single sample was injected on both systems to verify the reproducibility of the individual systems. In addition a full set of samples was analysed on both systems to evaluate the applied calibration of our analyzer (see Section 2.4).

2.3. Calibration of the instrument

Prior to daily analyses, alternating seawater and Milli-Q were injected on the catalyst until the baseline was stable. At the beginning and end of a daily run, the analyzer was calibrated against standard addition curves of potassium hydrogen phthalate (Baker) in Milli-Q and seawater. Standards (0, 50, 100 and 200 $\mu\text{M C}$) were prepared fresh every day from a stock solution of 1000 ppm C and injected in quadruplicate in an order of increasing concentration (alternating seawater and Milli-Q standards). The

beginning and end curve of a run were averaged and the slope of the seawater curve was used to calculate the organic carbon concentration in seawater samples. All samples were corrected for a blank calculated from the intercept of the Milli-Q curve with the x -axis. This blank actually consists of the apparatus blank and a water blank (carbon present in the Milli-Q), but in contrast to earlier studies (Suzuki et al., 1992) recent studies have shown, that Milli-Q usually contains little carbon and, consequently, can be used as essentially zero carbon water (Sharp et al., 1995; Carlson and Ducklow, 1995; Peltzer et al., 1996; Sharp, personal comm.). The organic carbon concentrations have to be considered as minimum estimates, since the reported values have been corrected for a blank, which is perhaps slightly overestimated. However, any underestimation is within the accuracy of the analytical method.

The instrument response factor, measured as the slope of the standard addition curve in seawater ($r > 0.99$ for 37 runs), remained relatively constant and reproducible over the course of more than a year. When calibration curves showed low reproducibility ($r < 0.99$) at the start of a run, no samples

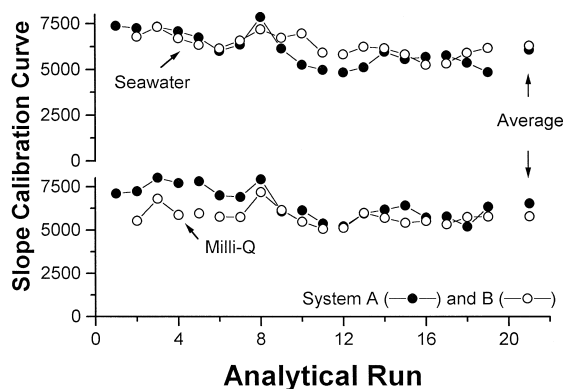


Fig. 3. Variance in the daily analyzer response factor of systems A and B, measured as the slope of four point standard addition curves of potassium hydrogen phthalate in seawater and Milli-Q. Plotted are the daily averages of the beginning and end of 37 runs ($r > 0.99$), at which ANTARES samples were analysed (February 1994–July 1995). The catalyst was regenerated after run 7. The offset between the seawater and Milli-Q slopes was in the order of 8%.

were analysed on that particular day. In general, calibration curves in seawater and Milli-Q exhibited slight differences in slope (Fig. 3; slope at beginning and end of the run averaged). The offset between the seawater and Milli-Q slopes was approximately 8% and was inconsistent when examining performance of the two columns on different runs. Since, the assessment of the apparatus blank from the peak area

of single small peaks has low precision, our blank was estimated from a four point calibration curve, rather than calculating the blank from single Milli-Q peaks. The blank was $27.4 \pm 5.4 \mu\text{M C}$ (range 18–39 $\mu\text{M C}$) and $15.2 \pm 7.7 \mu\text{M C}$ (range 5–32 $\mu\text{M C}$) for system A and B, respectively. Average analytical precision of the instrument was $\pm 4.6 \mu\text{M C}$ for triplicate injections ($n = 404$).

2.4. Method validations and comparisons

Since not all the analyses were made at sea, it was necessary to show that samples could be stored and returned to the shore laboratory without introducing any artefacts. Therefore, station A06 (66°S) was sampled in duplicate for analysis on-board and at the shore laboratory (15 months later). The results of the two determinations, plotted in pairs in Fig. 4a, fell close to the ideal 1:1 relationship. These small offsets suggest that it is justified to compare differences between the various stations.

It can be suggested that samples should have been run on one system rather than combining two, for consistency within the data set. Therefore, we conducted a second comparison. One set of 11 samples, distributed by J. Sharp for the second stage (1995) of the large community methods comparison of DOC (one sample was broken during transport to the

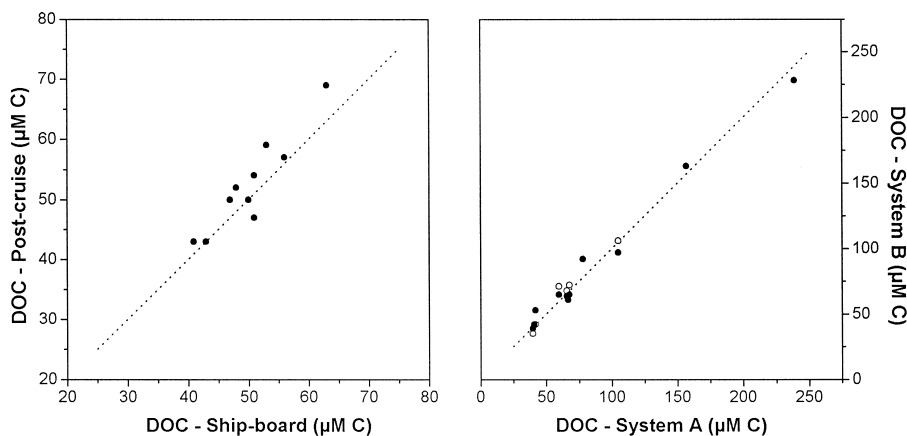


Fig. 4. Comparison of (a) ship-board and post-cruise analyses and (b) paired comparison between system A and B of the Ionics analyzer. Samples taken at station A06, were analysed on-board the R.V. *Marion Dufresne* and duplicate samples were analysed 15 months later at the shore laboratory. One set of 11 samples, distributed by J. Sharp for the second international intercalibration (1995), were analysed simultaneously on system A and B of the Ionics analyzer (closed symbols). Values were calculated with the slope of the standard addition curve in seawater and were corrected for the 'blank' water supplied by J. Sharp. For comparison with the classical WCO-method, seawater samples analysed on an OI-analyzer are included in the plot (open symbols). Dotted line represents 1:1 correlation.

Netherlands), were analysed simultaneously on system A and B of our analyzer (analyst identification no. 37). In addition, a second set of samples (40 ml) were analysed at our laboratory on an OI Model 700 Total Carbon analyzer (persulphate based oxidation (WCO) method described by Menzel and Vaccaro, 1964). Results of the many laboratories involved in the intercomparison will be dealt with by J. Sharp (personal comm.). The paired comparison between system A and B of the HTCO-analyzer, and between system A and the OI-analyzer are plotted in Fig. 4b. All sample concentrations have been corrected with the blank water supplied for the intercomparison (system A: $22.7 \mu\text{M C}$ and B: $22.9 \mu\text{M C}$). The average of the samples deviated by only $0.6 \mu\text{M C}$ between system A and B. The correlation line has a slope of 0.95 ± 0.04 and an intercept of 5.2 ± 4.1 . This line is statistically indistinguishable from the ideal correlation with a slope of 1 and an intercept of zero. Sea water samples analysed on the OI-analyzer were in good agreement with the results obtained with the HTCO-method. The average of seawater samples deviated by $2.1 \pm 5.7 \mu\text{M C}$ but fresh water samples had a higher offset. Our results are presented as evidence that system A and B did not yield significantly different DOC concentrations (also versus WCO-method) and should be directly comparable to recently reported HTCO-data.

Parallel to the Shimadzu integrator, the raw peak data was stored on a PC for later integration using an XCHROM[®] software package. To investigate the influence of peak integration on instrument performance we compared the Shimadzu and XCHROM analyses for the same set of samples. The samples ranged from 38 to $91 \mu\text{M C}$ ($\text{DOC}_{\text{XCHROM}} = 1.36 + 0.97 * \text{DOC}_{\text{Shimadzu}}$; data not shown). Although a strong correlation was observed ($r = 0.92$, $n = 104$), occasionally samples deviated considerably (up to $15 \mu\text{M C}$) from the regression line. This variance, solely introduced by different peak integration, is on the same order as the best results obtained in comparisons between HTCO analyzers (see Fig. 3 in

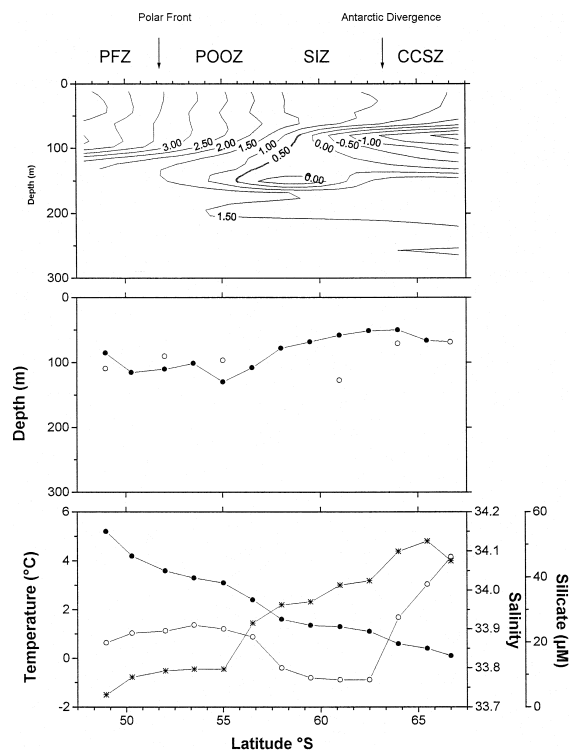


Fig. 5. Hydrographic characteristics of the 62°E meridian section: (a) contour plot of temperature, (b) depth of the mixed layer (filled symbol) and euphotic zone (open symbol), (c) surface temperature (filled symbol), salinity (open symbol) and silicate concentration (cross).

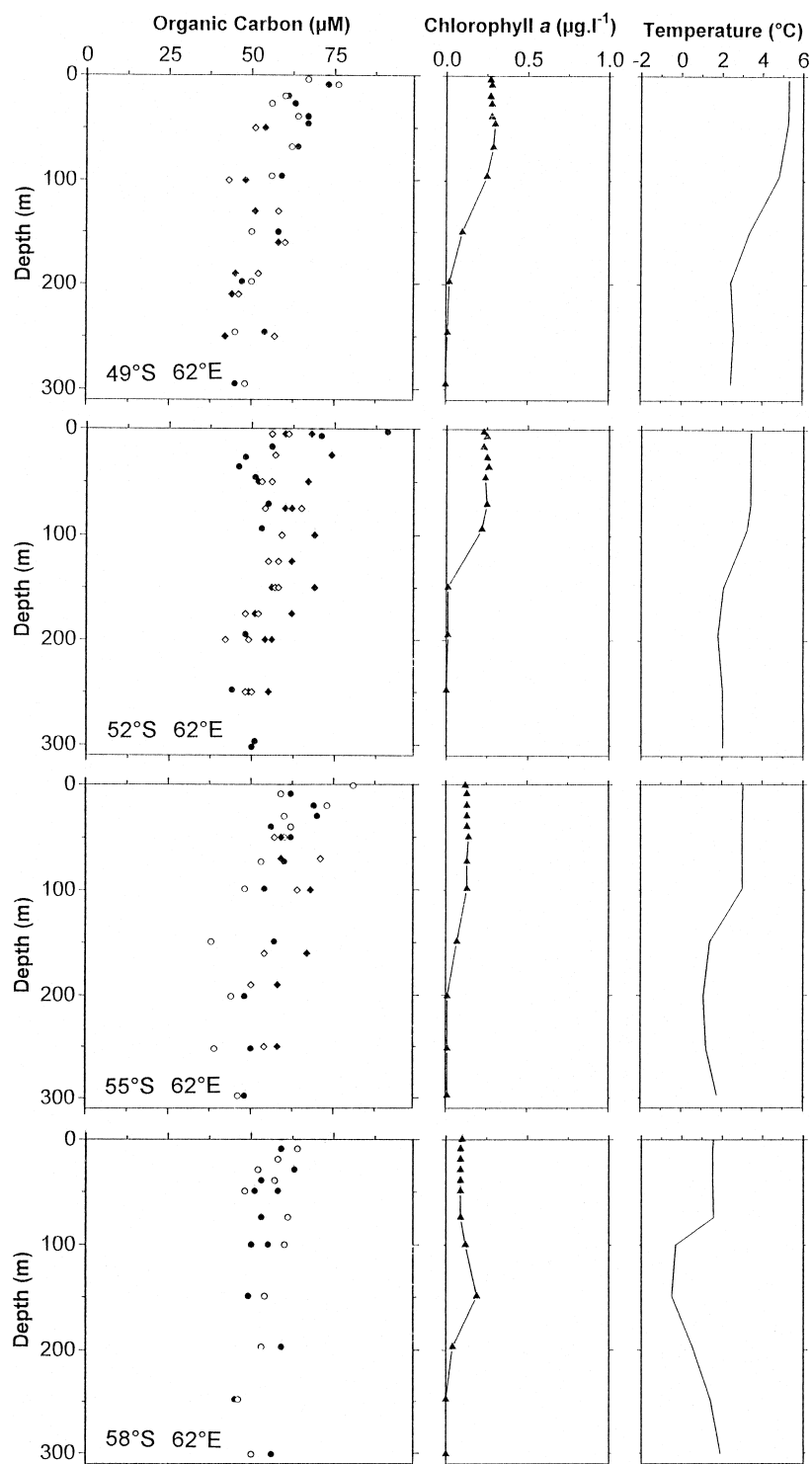
Sharp et al., 1995; Peltzer et al., 1996) or IR-detectors (Fig. 1 in Sharp et al., 1993).

3. Results

3.1. Hydrography

The section of the 62°E meridian covered by this study extended from the shelf of the Antarctic continent (860 m depth at southernmost station) into the PFZ, crossing the Antarctic Divergence at 63–64°S and the Polar Front at 52°S. Ice cover in winter

Fig. 6. Profiles of Organic Carbon (TOC closed symbols and DOC open symbols), chlorophyll *a* (triangle) and temperature at individual stations along 62°E over 49°S to 66°S interval. Chlorophyll data is courtesy of M. Fiala (Cruise report ANTARES 2/MD 78, Les publications de l'Institut Français pour la Recherche et la Technologie Polaires 95: 01).



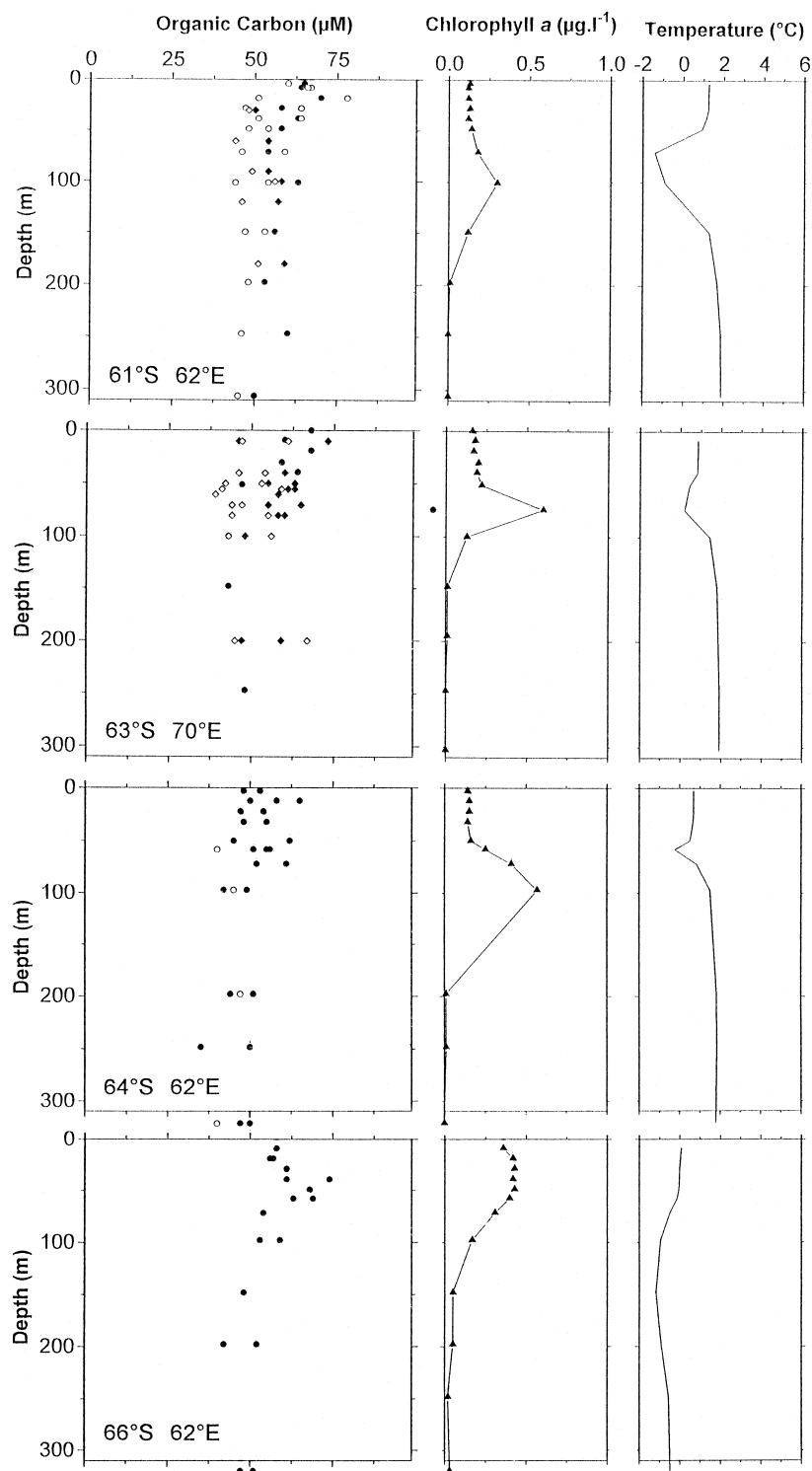


Fig. 6 (continued).

extends to 58°S but was completely retreated to the continent at the time of our study. Mean surface variables (temperature, salinity, nutrients) and physical characteristics of the water column along the transect are given in Fig. 5. Surface temperature gradually increased from 0°C in the south to approximately 5°C in the PFZ. The depth of the mixed layer varied from 40 m in the CCSZ to 130 m in the POOZ. Nutrient signature showed typical Southern Ocean values with surface nitrate ranging from 23 μM in the PFZ to 29 μM at the southernmost station, accompanied by a decrease in silicate from 51 to 4 μM . Stations south of the Antarctic divergence were characterized by cold and saline surface water and a rather uniform vertical temperature profile. In contrast, strong vertical temperature gradients, caused by relatively warm and less saline surface water overlying cold saline winter water, were present in the SIZ. The pronounced subsurface temperature minimum, deepened from 70 m depth in the south to 150 m near the POOZ.

3.2. Distribution of organic carbon

All data of TOC and DOC measurements at stations sampled from 0–300 m, are presented in Fig. 6. In a significant number of samples, the DOC concentration appeared to be greater than TOC. This artefact suggests some degree of contamination during filtration. However, filtration of our blank water (Milli-Q) resulted in $< 2 \mu\text{M C}$ deviation from the untreated Milli-Q water (applied three times over the course of the cruise). This is within the analytical precision of the analysis. The difference between TOC and DOC analysis represents the particulate organic carbon (POC) fraction, which was on average $2.2 \pm 5.6 \mu\text{M C}$. Since average POC values (0–150 m) ranged from 3–6 $\mu\text{M C}$, as determined by A. Bedo (Fiala, 1995), we assume a negligible contribution of POC to the total organic carbon and, therefore, consider all analysis as DOC values. Duplicate TOC and/or DOC analyses (if applicable) were averaged for further calculations.

At several stations (A18, A01, A14, A10, A04) additional GOFLO casts were sampled (plotted in Fig. 6 as diamonds). The resulting profiles were slightly different, thereby contributing to the scatter in the vertical profiles. DOC concentrations were

slightly elevated in the upper 100 m compared to underlying waters. Except for one cast at station A04, which showed a clear correlation between chlorophyll *a* and DOC (105 $\mu\text{M C}$ at 75 m depth), there were no other subsurface DOC maxima corresponding to the deep chlorophyll *a* maximum (DCM) present at stations near the Antarctic Divergence. Along the 62°E meridian, average DOC concentration in the top 100 m ranged from 51.5 to 63.2 $\mu\text{M C}$ (43–91 $\mu\text{M C}$ for individual samples) and decreased to an average of $47.6 \pm 2.5 \mu\text{M C}$ by 200–300 m ($n = 22$). The DOC inventory (mmol C m^{-2}) over 100 m depth intervals is presented in Fig. 7. The DOC concentration in the mixed layer was highest in the PFZ and decreased to the south but no strong gradients were observed. At the continental shelf of the Antarctic continent (900 m depth) the DOC concentrations in surface water increased again.

A composite of TOC profiles at the stations sampled down to the bottom is presented in Fig. 8. Profiles show a slight decrease of TOC concentration with depth, from a maximum of 91 $\mu\text{M C}$ in surface water to an average of $42.2 \pm 4.3 \mu\text{M C}$ below 2000 m. The profiles show considerable scatter and there is no pattern with latitude in the deep water with the possible exception of the northernmost station (PFZ),

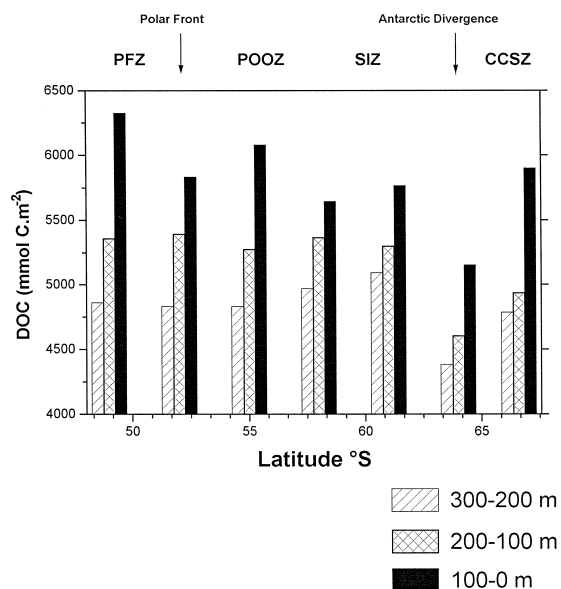


Fig. 7. Integrated DOC inventories (mmol C m^{-2}) along the 62°E meridian over 100 m depth intervals.

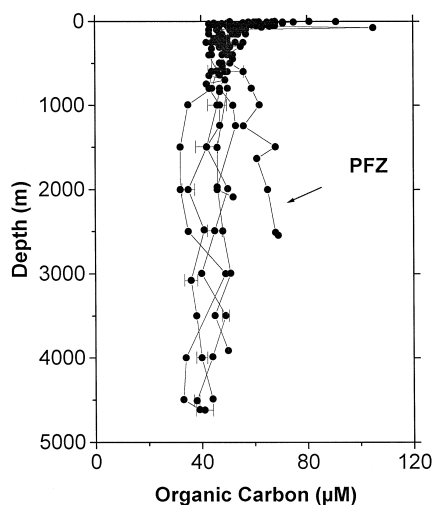


Fig. 8. Composite of deep vertical profiles of Organic Carbon ($\mu\text{M C}$) at six stations (A01, A04, A10, A12, A14 and A18). Error bars indicate duplicate analysis of in total 12 deep water samples of station A10 and A12.

which is situated above the Kerguelen ridge (2610 m depth). The PFZ deep water values do appear to be higher than those of the other station; however, the values from 500 m are not higher.

4. Discussion

Since the special issue of *Marine Chemistry* on the measurement of DOC and dissolved organic nitrogen in natural waters (volume 41, 1993), the effort of many researchers has improved the analysis of DOC in seawater. There have been several papers which have discussed the HTCO method and evaluated instrument performance. The accuracy of an HTCO-analyzer is directly dependent on the combustion efficiency, the peak integration and a reliable blank correction. Recent papers give emphasis to the possibility that discrepancies among various analysts and methods may, at least partially, be due to improper estimate of the blank (Sharp, 1993; Sharp et al., 1993; Peltzer et al., 1996). Critical evaluations of the analytical blank show that the catalyst has a major contribution to the blank (Benner and Strom, 1993; Cauwet, 1994). Recently, several intercomparisons showed improvement in accuracy and precision of the HTCO-method (Sharp et al., 1993). However,

the accuracy between participating laboratories is consistently higher than the individual precision (Sharp, personal comm.).

With the use of a Li-Cor CO_2 -analyzer, proven to be more stable and accurate in $p\text{CO}_2$ measurements ($\pm 0.1 \mu\text{atm}$) by many ocean going research groups, we obtained a stable base-line, which improved peak integration irrespective of the motion and vibrations of the research vessel (Peltzer and Brewer, 1993; Sharp et al., 1993; Tupas et al., 1994). Part of the variation of our DOC analyses can be explained by inadequate integration of non-ideal peaks, although peaks showed only slight visual tailing and none of the peaks were of irregular shape. Apparent inconsistency among HTCO-analyzers could be due to differences in peak detection and integration rather than differences in combustion systems (Sharp et al., 1993).

Despite extensive conditioning of the catalyst (Sharp et al., 1993), a slight difference ($\sim 8\%$) in instrument performance between the solvents for the standards remained (Fig. 3). Although similar matrix effects have been reported previously (De Baar et al., 1993), this variability has not been studied in detail. Our blank values are consistent with those of other groups which used a similar Ionics set-up ($18.7 \pm 1.5 \mu\text{M C}$ by Tupas et al., 1994; $> 30 \mu\text{M C}$ by Sharp et al., 1995). Sharp et al. (1993) report blanks of $9\text{--}35 \mu\text{M C}$ for four commercial HTCO analysers, using different catalysts. Chen and Wangersky (1993) report a blank of $15 \pm 5 \mu\text{M C}$, of which the major contribution was from the analytical system and not the carbon content of the original water. Extensive 'steam cleaning' of the catalyst bed is required to get the blank value of the often used platinized-alumina catalyst below $25 \mu\text{M C}$ (Benner and Strom, 1993). Platinized-quartz catalysts appear to yield lower blank estimates (Copin-Montégut and Avril, 1993; Thomas et al., 1995), but easily disintegrate on repetitive seawater injection, making them unsuitable for routine analysis of seawater samples (Benner and Strom, 1993; Cauwet, 1994). Differences between the two independently calibrated systems of our analyzer were within the precision of the method ($\pm 4.6 \mu\text{M C}$) and our results of the most recent large community DOC-method comparison (1994, 1995), conducted by J. Sharp were in agreement with other analysts (Sharp, personal comm.). Therefore we have

confidence that our calibrations give close to real estimates of DOC concentrations.

4.1. Surface distribution of DOC

The average DOC concentrations in the mixed layer, ranging from 51.5 to 63.2 $\mu\text{M C}$, are consistent with the most recent results of the Southern Ocean (Wedborg et al., in press; Carlson, personal comm.) but are slightly lower than the best estimates of surface DOC concentrations in other oceans: equatorial Atlantic Ocean 62–97 $\mu\text{M C}$ (Thomas et al., 1995); equatorial Pacific Ocean 62–72 $\mu\text{M C}$ (Carlson and Ducklow, 1995) and 60–80 $\mu\text{M C}$ (Peltzer and Hayward, 1996), northwestern Sargasso Sea 64–71 $\mu\text{M C}$ (Carlson et al., 1994). Slightly elevated DOC concentrations in the mixed layer, compared to deep water, indicate low net production of DOC. This means that DOC produced by food web processes is tightly coupled to DOC utilization by heterotrophic processes. Therefore, the majority of the ‘freshly’ produced DOC should be readily available for consumption by bacterioplankton and only a small fraction escapes mineralisation and accumulates in the mixed layer. The accumulating DOC, consisting of semi-labile material which turns over on a seasonal time scale, accounts for 18–33% of the bulk DOC in the top 100 m (assuming an equal distribution of the refractive DOC pool throughout the water column). Carlson and Ducklow (1995) calculated this pool to account for approximately 40% of the bulk DOC in the mixed layer of the equatorial Pacific Ocean (equivalent to approximately 30% in the top 200 m). Apparently, up to twice as much DOC escapes mineralisation and accumulates at their site.

Spring phytoplankton blooms, associated with the retreating ice edge (Smetacek et al., 1990), result in higher annual productivity in the vicinity of the Antarctic Divergence and the SIZ, compared to the POOZ. In summer, when the biologically labile DOC has been utilised by heterotrophic process, the semi-labile DOC pool will remain. If a constant fraction of primary production will end up in the semi-labile DOC pool, the higher annual productivity in the south should result in higher DOC concentrations in summer. However, we see an opposite trend along the 62°E meridian, with highest DOC concentrations

in the PFZ decreasing to the south by 11.7 $\mu\text{M C}$ (Fig. 7). The lower DOC in the south indicates removal of semi-labile DOC on relatively short time scales (weeks to few months) by heterotrophic processes or advective transport.

In an oceanic system, the carbon demand of bacterioplankton, ultimately supplied by primary production, has to be channelled through the labile fraction of the DOC pool. During ANTARES 2, the low primary production could only sustain low bacterial production. Assuming a growth efficiency of 50%, bacterioplankton demand was on average 4 $\text{mmol C m}^{-2} \text{ d}^{-1}$, equivalent to approximately 30% of the primary production (Table 2). Apparently, the daily turnover of the labile DOC pool is only a small fraction of bulk DOC in the euphotic zone. In Fig. 9, DOC accumulated in the mixed layer, calculated from the difference between integrated DOC in the upper 100 m and the underlying 100–200 m, is compared with corresponding measurements of phytoplankton biomass (chlorophyll *a*) and bacterial production. Except for the station at 55°S (A14), the elevated DOC concentration in surface water showed a clear trend with standing stocks of phytoplankton and bacterial production. Increased bacterial productivity appears to result in accumulation of DOC in the mixed layer. Although the trend between bacterial production and semi-labile DOC might be merely coincidental, the interesting question remains whether the semi-labile DOC is produced by the bacteria

Table 2
Depth integrated primary and bacterial production and carbon stocks along the 62°E meridian

Property	($\text{mmol C m}^{-2} \text{ d}^{-1}$)	Source
Primary production	5.8–20.8	Lancelot et al., 1995
Bacterial production	1.7–6.3	Talbot, 1995
Excess DOC ^a	278–961	This study
Carbon stocks (mmol C m^{-2})		
Phytoplankton (0–150 m)	27.2–171.4	Fiala et al., in press
Bacterioplankton (0–150 m)	62.3–125.0	Talbot, 1995
DOC (0–100 m)	5153–6324	This study

^aExcess DOC in mixed layer: calculated as the difference between integrated DOC in the upper 100 m and the 100–200 m depth interval.

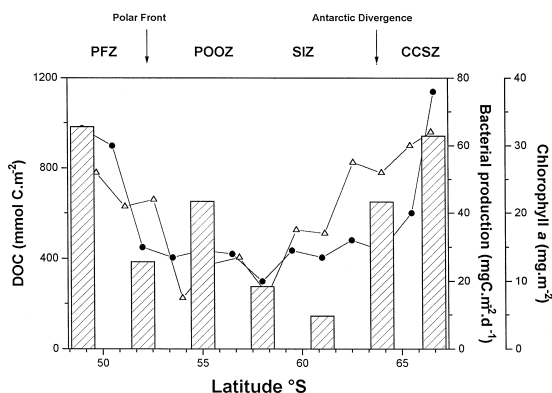


Fig. 9. Trend between carbon stocks and biological activity along 62°E. Excess DOC in surface water compared to underlying water (calculated as the difference between integrated DOC in the upper 100 m and the 100–200 m depth interval) is indicated with bars, bacterial production (circle) and chlorophyll *a* (triangle). Bacterial data is courtesy of V. Talbot (*Activité protéolytique et dynamique bactérienne en Océan Austral*. PhD thesis 1995, Marseille, 194 pp.). Phytoplankton data is courtesy of M. Fiala (*Cruise report ANTARES 2/MD 78*, Les publications de l'Institut Français pour la Recherche et la Technologie Polaires **95**: 01).

themselves, rather than left behind after utilization of the biologically labile DOC pool.

The southernmost station (A06) on the continental shelf of the Antarctic continent (CCSZ) deviates considerably from the general trend along the 62°E meridian. Low surface temperature and high salinity indicate suitable conditions for deep water formation. Runoff from the continent with high organic load is reflected in relatively high DOC and POC concentrations in surface water (59.0 and 5.5 $\mu\text{M C}$, respectively). In the Antarctic Divergence and the SIZ strong vertical temperature gradients indicate a stable water column. Associated with the temperature minimum, a pronounced subsurface maximum in phytoplankton biomass existed, as is apparent from the high chlorophyll *a* (Fig. 6). However, DOC, POC and bacterial production profiles were not affected. Phytoplankton in the maximum were actively photosynthesising, as is reflected in more negative $\delta^{13}\text{C}$ of POC (Dehairs et al., 1995). Apparently this did not result in additional production of labile and/or semi-labile DOC at this depth. This might explain why bacterial production was in general high in surface water decreasing with depth without additional subsurface maximum (station A04, A08, A09, A11 and A12; see Talbot, 1995).

4.2. DOC in relation to mesopelagic and deep water mineralisation

The DOC anomaly in deep water of the PFZ (station A18) coincides with the salinity maximum and nutrient minimum of the Lower Circumpolar Deep Water (LCDW), which derives from the North Atlantic Deep Water (NADW) (Whitworth and Nowlin, 1987). Salinities greater than about 34.73 show the influence of this NADW introduced south of the Polar Front into the SIZ (Fiala, 1995). However, from the DOC profiles there is no evidence for the existence of a tongue of high DOC in deep water extending south from the Polar Front (Fig. 8). Therefore, we conclude that there is no evidence for advective import of high DOC from the NADW. Anomalously high DOC concentrations, approaching mixed-layer concentrations, have also been reported for the Weddel Sea (Wedborg et al., in press), equatorial Atlantic and Pacific Ocean (Thomas et al., 1995; Peltzer and Hayward, 1996). Patches of high TOC concentrations were interpreted to result from mass sinking of phytoplankton blooms or horizontal advection of high DOC water. The origin of high DOC in deep water remains unresolved.

Considering the relation between DOC and apparent oxygen utilization (AOU; difference between theoretical saturation and measured dissolved oxygen concentrations) can give additional insights in the respiration and decomposition of organic matter below the mixed layer. From the strong correlation between DOC and AOI it has been suggested that the decomposition of DOC may be responsible for oxygen depletion in the deep sea (Sugimura and Suzuki, 1988). However, this data have been retracted (Suzuki, 1993). Menzel and Ryther (1968) argued against respiration and decomposition of organic matter at depth and thus for a 0% correlation. Weak or insignificant correlations between DOC and AOI have been reported for the equatorial Pacific (Martin and Fitzwater, 1992), the Indian Ocean (Kumar et al., 1990) and North Atlantic (De Baar et al., 1993) and deep samples of the North Pacific Gyre (Williams and Druffel, 1987).

In Fig. 10, values for DOC are plotted against AOI. The lack of fit of the PFZ deep water samples (A18) is further, albeit serendipitous, evidence that they may be analytical artefacts. Following a Model

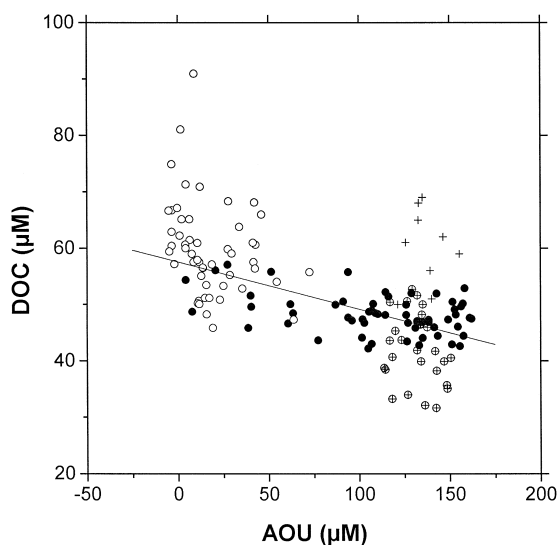


Fig. 10. Correlation of DOC vs. AOU. Geometric mean Model II linear regression for samples (●) collected from depths between 100 and 1000 m: slope = -0.084 ± 0.010 , intercept = 57.5. Data for samples (○) in the mixed layer (100 m) and (⊕) below 1000 m. Deep water samples (+) in the PFZ (station A18).

II linear regression approach (Ricker, 1973; Laws and Archie, 1981) for samples, limited to depths between 100–1000 m, the slope of the geometric mean was -0.084 ± 0.010 and the intercept 57.5. However, the slope was not significantly different from zero ($n = 59$). This is consistent with the -0.074 ($r = 0.89$) recently reported for the equatorial Pacific Ocean (Peltzer and Hayward, 1996) and the -0.14 ($r = 0.86$) and -0.09 ($r = 0.63$) reported for the equatorial Atlantic Ocean (Thomas et al., 1995). The slope was well below the $\Delta C:\Delta O_2 = 106:138$ after Redfield et al. (1963) and suggests that only a small fraction ($< 10\%$) of the oxygen consumption in the open ocean would be due to remineralization of DOC. In case of the Southern Ocean mineralisation of sinking particles might as well be the only contributor to the in situ utilization of oxygen. Depending on the geographical position, DOC in the mixed layer will accumulate to a different extent, while oxygen is assumed to be in equilibrium with the atmosphere. Therefore, mixed layer values plotted in Fig. 10 are in general above the geometric mean regression line. In contrast, deep samples are typically below the geometric mean (see also Peltzer and Hayward, 1996). Assessment of

horizontal gradients of DOC within the same water mass would yield better estimates of the contribution of mineralisation of DOC to oxygen consumption in deep water.

4.3. DOC in deep water

We estimated the DOC of deep water in the Southern Ocean to average at $42.2 \pm 4.3 \mu\text{M C}$, which is in good agreement with the $36\text{--}39 \mu\text{M C}$ reported for the equatorial Pacific Ocean (Carlson and Ducklow, 1995; Peltzer and Hayward, 1996) and slightly lower than $48 \pm 6.6 \mu\text{M C}$ in the equatorial Atlantic (Thomas et al., 1995). This low deep water DOC is confirmed by recent intercalibrations for which several deep water samples, from different oceans, have been analysed (Sargasso Sea $40\text{--}50 \mu\text{M C}$ by Sharp et al., 1993; equatorial Pacific Ocean $35\text{--}40 \mu\text{M C}$ by Sharp et al., 1995; North Atlantic Ocean $47\text{--}55 \mu\text{M C}$ by Peltzer et al., 1996). The HTCO-values cited here have in common that the apparatus blank was carefully evaluated and samples were corrected accordingly. However, they are not all totally consistent in the blank correction, e.g., in some cases, the blank water was assumed to have or actually shown to have a slight DOC content. Therefore, these offsets may simply be due to blank correction and the true values might be closer. Virtually all papers reporting high HTCO-values in the deep sea (see citations by Peltzer et al., 1996), were published at a time when no blank correction was made. The consistency in low deep water values, homogeneously distributed over the different ocean basins, provide evidence for a constant deep-water DOC concentration comprised of biologically resistant material. This resembles the apparent old radiocarbon age of deep water DOC, with lifetimes on the order of the turn-over time of the global ocean (Williams and Druffel, 1987). Because there has been no set reference standard, the average deep DOC concentration could be used as a first approximation to validate comparisons between different data sets.

4.4. Summary

Despite the large standard deviation of the DOC analysis we were able to distinguish trends in DOC

concentrations in relation to biological activity. The Southern Ocean is characterized by low DOC concentrations in surface waters. South of the Polar Front, profiles show a decrease with depth to approximately 42 μM C below 2000 m. Increased productivity resulted in slight accumulation of DOC in the mixed layer. This semi-labile DOC pool, accounting for 18%–33% of the bulk DOC in the top 100 m, appears to turn over within weeks to a few months. The subsurface maximum in phytoplankton biomass, as apparent from increased chlorophyll *a*, present in the SIZ was not reflected in the DOC profile. From this we conclude that the phytoplankton in the maximum, although photosynthetically active, did not contribute significantly to the carbon fluxes in the water column. This is confirmed by measurements of POC and bacterial production. Mineralisation of deep water DOC accounts for less than 10% of the oxygen consumption, as appears from the correlation between DOC concentration and AOU.

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